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Ionization energy of the shallow nitrogen acceptor in zinc selenide

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Evidence on the presence and binding energy of the shallow N acceptor is obtained for growth-doped liquid-phase-epitaxial (LPE) and organometallic chemical-vapor-deposited (OMCVD) ZnSe thin single-crystal layers. The small increase in N-acceptor bound-exciton (BE) binding energy E_{BX} relative to the Li acceptor, 0.3 meV, is clearly established from intercomparison of spectral features and use of tunable dye-laser spectroscopy. The LPE crystals contain a new unidentified donor $E_D=26.8$ meV, as well as In and Al minor donors, while the dominant donor in these OMCVD crystals is Ga. Selectively excited donor-acceptor-pair (DAP) luminescence spectra contain a satellite structure which provides an estimate of $(E_A)_{\mathrm{N}}=111\pm1$ meV, distinctly 2.2 ± 0.5 meV shallower than the Li acceptor but ~21 meV deeper than some previous estimates from LPE ZnSe:N. This estimate is confirmed by A^0,X BE "two-hole" satellites observed under strong optical pumping. The effective-mass value of E_A is placed close to 110 meV. The dependence of displacement energy of this structure on DAP separation is very significant in the comparison of Li and N acceptors. The relationship of E_{BX} and E_A is retrograde for the shallowest acceptors N, Li, and Na so far identified in ZnSe. Sharp differences between the excitation spectra of BE photoluminescence between *n*-type ZnSe and *p*-type ZnTe doped to comparable concentrations are discussed. It is concluded that the best N-doped OMCVD ZnSe yet available is still *n* type due to residual donors.

I. INTRODUCTION

Zinc selenide has long been recognized as one of the most promising II-VI semiconductors for optoelectronic device applications. In particular, as a light emitter it has several nearly optimum properties, including a direct band gap near 2.7 eV, just large enough to provide blue as well as longer-wavelength recombination luminescence. Zinc sulfide can also produce blue as well as other color luminescence, all as a result of recombination through *deep* states. However, the much larger band gap of ZnS brings with it additional difficulties of control of impurity incorporation and native defects resulting from the significantly larger growth temperature and also the larger energy gain on compensation. These properties exacerbate inadvertent compensation phenomena produced in reaction to deliberate attempts to control electrical conductivity.[1] It is well known that ZnSe can be made *n* type with quite useful conductivity through conventional vapor transport or bulk growth and subsequent anneal in Zn-excess conditions[2,3] by liquid-phase expitaxial (LPE) growth using as background dopants suitable group-III donor dopants in the growth solvent,[4] or by organometallic (OM) chemical-vapor deposition with the donor provided through a suitable metal alkyl such as triethylaluminium.[5] Resistivities of $<0.1\ \Omega\,\mathrm{cm}$ can be obtained by all these methods, but with particularly low compensation using the OM technique.

Production of *p*-type ZnSe is well known to be very difficult. One of the main reasons is the lack of suitably well-behaved acceptor species. These problems were first clearly exposed for CdS,[6] a II-VI compound semiconductor with properties and problems remarkably similar to ZnSe. Henry *et al.*[6] demonstrated that use of the obvious cation-site shallow acceptors Li and Na is frustrated by amphoteric doping involving an interstitial species of low stability. Lithium is the most amenable acceptor because the cation solubility decreases rapidly with ionic radius of the group-I species, so that K appears to be completely insoluble even in CdS. Neumark and Herko[7] have recently shown that the achievement of useful concentrations of substitutional Li acceptors is frustrated in ZnSe to at least the same extent as it is in CdS.[6] The best possibility involves rapid quenching from high growth temperatures. However, problems of control of other deep centers then arise. The use of high electric drift fields suggest that the $\mathrm{Li_{Zn}}$ acceptor as well as the interstitial-donor ($\mathrm{Li_I}$) may be unstable under conditions normal near the junction of a *p-n* diode.[7] Thus although $\mathrm{Li_{Zn}}$ and $\mathrm{Na_{Zn}}$, respectively, have acceptor ionization energies $E_A\sim114$ (Ref. 8) and 128 meV (Ref. 9) suitably small for the promotion of efficient electrical conductivity at 300 K, use of these acceptors so far remains frustrated by these other problems. Among the possible group-V anion-site substitutional acceptors, P and As apparently undergo large static displacements from the T_d-symmetry Se lattice site.[10] The consequent enhancements in E_A to ~0.6 eV removes interest in these species for promoting electrical conductivity at 300 K. Clear evidence has been obtained for a much shallower acceptor, $E_A \sim 90$ meV, in ZnSe:P.[4,11] However, this species seems active only at large doping levels. It has not yet been proved possible to obtain crystals in which the concentrations of P-related and other deep acceptor levels (Cu is a particular problem) are sufficiently low to allow the hole Fermi level to be controlled by this or any other shallow species.[12] The 90-meV acceptor probably involves some complex containing P rather than a simple point defect.

These considerations isolate N as the only plausible *shallow* substitutional acceptor in ZnSe, like CdS. This was recognized by Henry *et al.*,[6] who realized that the strong differential electronegativity of N and S should ensure that N_S would be shallow. They could not produce successful N doping of CdS using vapor-transport growth, however. Recent attempts to incorporate N in LPE ZnSe were successful to a limited degree.[4,13] The problem was that many crystals contained more Li than N and also the deep Cu acceptor was invariably present. Codoping by Li raised difficulties in the demonstration of successful incorporation of N through the neutral acceptor bound excitons (BE) (A^0,X BE or I_1 lines), since I_1^{Li} and I_1^{N} are separated by only 0.3 meV, rather comparable with the individual BE linewidths in the best LPE crystals. This problem stems from the lack of sensitivity of the A^0,X BE localization energy E_{BX} to differences in E_A for shallow acceptor species, now well recognized in direct-gap semiconductors like ZnSe.[14] Emphasis is, therefore, thrown on the distant donor-acceptor—pair (DAP) luminescence process, at least for the derivation of E_A if not also for the recognition of the new acceptor species. Unfortunately, the best N-doped LPE crystals prepared by growth doping[4,13] or ion implantation[15] contain rather large doping densities. Under these conditions, and especially for high-optical excitation rates used in the previously published work,[4,15] the DAP bands become rather broad. A particular problem for ZnSe is the "intermediate association" effect in the relative donor and acceptor site distributions, believed to be a special characteristic of a DAP system with a low-temperature mobile species such as $\mathrm{Li_I}$.[16,17(a)] This phenomenon has recently received careful analysis.[17(b)] However, the consequence for the present work is that it is now believed that the upshifted DAP band previously identified[4,13,15] with a $\mathrm{N_{Se}}$ acceptor with $E_A \sim 20$ meV less than $(E_A)_{\mathrm{Li}}$ results from distortions in the DAP intensity envelope caused by intermediate association or a free-electron—to—bound-hole transition. This conclusion is strongly supported by recent work on organometallic chemical-vapor-deposited (OMCVD) ZnSe:N,[18] where the concentrations N_A and N_D were sufficiently small to promote narrow DAP spectral peaks. The residual Li contamination is generally significantly smaller in low-temperature-grown OMCVD ZnSe compared with LPE ZnSe, which minimizes the possibility of intermediate association effects if they are a particular feature of Li_I donors.

This paper reports a careful study of ZnSe:N grown by both OMCVD and LPE techniques, using a tunable dye laser for selective excitation of both the BE and DAP luminescence. Usually, information on any shallow acceptor such as $\mathrm{N_{Se}}$ can best be obtained using selectively excited photoluminescence (SPL). If the laser energy is tuned to the dominant lowest-energy component of the N A^0,X BE no-phonon line, $(E_A)_{\mathrm{N}}$ may be derived from the series of "two-hole" BE satellites[14] which can be resonantly enhanced under these conditions.[19] However, because even the best spectroscopic samples of N-doped ZnSe remain *n* type and since the A^0,X BE lies below the energy threshold $(E_G - E_D)$ for efficient optical generation of free holes, we show that optical pumping of the A^0,X BE luminescence is best achieved under intense above-band-gap excitation. The higher N doping required to achieve high-resistivity *p*-type material inevitably broadens the spectral features[4,13] beyond recognition. The displacement energy to the well-defined two-hole transition A^0,X BE satellite involving the 2*s*-acceptor excited state is 2.9±0.5 meV less than that for the Li acceptor, so that $(E_A)_{\mathrm{N}} = 111 \pm 1$ meV. Alternatively, SPL spectra of DAP transitions contain satellites also spaced by acceptor (as well as donor) internal excitation energies below the energy of the narrow laser line, which selectively excites DAP with a rather narrow range of internal separations *R*.[20] These techniques both give $(E_A)_{\mathrm{N}}$ about 3 meV less than $(E_A)_{\mathrm{Li}}$, i.e., about 111 meV. Consequences of this for the effective-mass theory value $(E_A)_{\mathrm{EMT}}$ for ZnSe are discussed.

II. EXPERIMENTAL

Two types of ZnSe single crystals were used in these measurements. The first was grown by LPE from Bi solution onto ZnSe single-crystal substrates obtained from the Eagle Picher Industries, Inc.[4] The layers were grown at about 900 °C and doped with N using NH_3 in the atmosphere surrounding the graphite sliding boat of the type familiar in the LPE growth of GaAs. The second type of crystals was prepared by OMCVD onto ⟨100⟩-oriented GaAs single-crystal substrates which provide a tolerably close lattice match to ZnSe.[5] The Zn and Se were provided by dimethyl Zn and H_2Se, respectively, and N was again added from NH_3.[18,21] A key feature of this growth technique, besides doping flexibility, is the very low growth temperature it provides, close to 350 °C in this work. This low temperature has important consequences in the growth of pure ZnSe relatively free from the presence of stoichiometric defects. These defects are notoriously responsible for deep centers in ZnSe which compensate shallow electrically active centers, in addition to chemical species such as Cu.[12]

Photoluminescence was mostly excited by a liquid-jet tunable dye laser using Stilbene III dye and pumped by 360-nm light from a Coherent Radiation 3000K Kr^+ laser, linewidth 0.1 meV. The spectrally narrow exciting light could be tuned from significantly above the band gap of ZnSe near 2.82 eV at 4 K to just above the shallow distant DAP peak energy near 2.70 eV. The average power was ~50 mW after the optical chopper necessary for detection of the signal with a GaAs photomultiplier and a lock-in amplifier. For intense above-band-gap excitation, the uv line of an Ar^+ laser was used. The luminescence was analyzed either by an f/17 2-m Baird Atomic spectrograph with a computer-controlled photoelectric scanning attachment[22] or with an f/7 0.85-m Spex double monochromator. Most of the crystals were freely suspended in liquid He at 4.2 K.

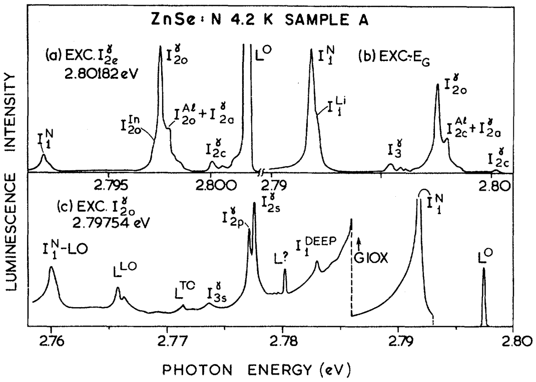

FIG. 1. Near-gap low-temperature photoluminescence from a homoepitaxial single crystal of ZnSe grown by liquid-phase epitaxy, sample *A* (646H:N), and doped with N, obtained under the indicated different energy settings of the tunable dye laser, which appears as L^0 in some of the spectra. The notation is usual for BE in II-VI semiconductors. I_1 is an A^0,X BE, I_2 at D^0,X BE. Superscripts denote the chemical species responsible for the *D* or *A* where known. γ is an unidentified donor. Subscripts $2o$, $2a$, $2c$, $2e$ indicate different states of the D^0,X BE; *o* is the ground state, *a* and *e* are excited states. Subscripts $2p$ and $2s$ in (c) denote two-electron transition satellites enhanced under resonant excitation into I_{2o}^{γ}. LO-phonon replicas also appear; L^{LO} is a Raman line. A change of recording sensitivity is denoted by *G*.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Bound exciton effects

The BE photoluminescence from the highest quality LPE crystal of ZnSe:N (Fig. 1) contains a number of recognizable features. The most straightforward is the sharp line at 2.7829$_3$ eV [Fig. 1(c)], very close to the accepted energy for the persistent I_1^{deep} BE line in strain-free dilutely doped ZnSe.[22] This has been identified with the A^0,X BE introduced by deep Cu_{Zn} acceptors.[11,12] The negligible energy shift of this line provides important evidence that the unequal doublet near 2.792 eV [Fig. 1(b)] cannot arise simply from a strain-shifted and slightly split version of the I_1^{Li} A^0,X BE attributed to the shallow Li acceptor, $E_A = 114$ meV.[8,9] Indeed, the weaker upper component of this doublet is at 2.7921$_3$ eV, very close to the normal energy of I_1^{Li}, whereas the stronger component falls at 2.7918 eV, some 0.3 meV below I_1^{Li}. This latter component correlates with the introduction of N during growth[4,13] or by ion implantation,[15] and has been interpreted as the I_1^{N} A^0,X BE. The rather small magnitude of this barely resolved spectral shift necessitates great care in establishing whether I_1^{N} is really introduced by N doping rather than being an artifact of the effect of crystal strain on I^{Li}. Such small strain or doping-related energy shifts of BE lines occur quite frequently in LPE ZnSe. However, the persistence of this shift in several crystals where the upper component is isoenergetic with the I_1^{Li} BE due to inadvertently present Li acceptors strongly supports the identification given in Fig. 1(b). For example, compressive strain shifts these BE lines to higher energy.

Selective excitation in the I_2 D^0,X BE can provide a useful cross check, since the displacement energies to the "two-electron" satellites thereby enhanced [Fig. 1(c)] should identify the donor species, and the energy of the main I_2 line can then be checked against the known energy for this species in unstrained ZnSe.[22,23] Unfortunately, this scheme is complicated by the fact that the dominant donor in this particular ZnSe crystal has 1*s*-2*s* and 1*s*-2*p* excitation energies, respectively, 19.8_3 and 20.2_9 meV. These energies lie between the values recognized for Cl and Ga donors in ZnSe and slightly closer to the latter. This new donor, labeled γ in Fig. 1(b), is so far unequivocally unidentified. B and Br are obvious possibilities, although the former has already been tentatively identified with a donor 0.3 meV shifted from an Al donor.[12] Perhaps it is due to Br, which could be incorporated during the heat-treatment cycle after the bulk ZnSe has been etched using Br-methanol. Ivanova *et al.*[23(b)] have recently observed a new donor essentially at the same position as the γ donor. They attribute this to a D^0,X BE transition at a complex of singly charged $(V_{\mathrm{Se}}^{2+}\text{-}\mathrm{Li}_{\mathrm{Zn}}^{-})^{+}$ donor. All we can say for the present purpose is that the energy of the I_2 D^0,X BE, 2.7975_3 eV [Figs. 1(a) and 1(b)] is roughly consistent with the value of E_D deduced from these two-electron satellites (26.8 meV) according to the Haynes rule between E_{BX} and E_D, which is known to hold for shallow donors in ZnSe.[23(a)] This is supported by the observation of weak I_2 components due to donor species In and Al, minor dopants in this crystal. These components fall close to the known D^0,X BE energies for these species,[22] confirmed from two-electron satellites with appropriate displacement energies. These satellites were best observed when the dye laser was tuned into their parent I_2 lines, rather than into those of the γ donor as in Fig. 1(a) and particularly Fig. 1(c). Strain and other perturbations are, therefore, negligible for this crystal, at least in the small region selected for these photoluminescence measurements.

This interpretation of the shallow I_1 BE receives strong support from the photoluminescence spectra of OMCVD ZnSe:N. Although the spectral lines are rather broad [Fig. 2(a)], the I_1^{N} component appears on N doping close to 2.7920 eV, consistent with Fig. 1(b). Our results are not perfectly consistent with the previous paper on the same material[21] with respect to BE transition energies, since we find all spectral lines including the free exciton (FE) downshifted by ~2—3 meV compared with high-quality bulk ZnSe, both as reported earlier[22] and as measured in the present work to establish a cross check. The exact value of the shift depends on the particular ZnSe layer investigated. This effect occurs for undoped or lightly doped OMCVD ZnSe grown on GaAs ⟨100⟩ both at Xerox Palo Alto Research Center and at Royal Signals and Radar Establishment and is believed to be a consequence of tensile crystal strain arising from lattice mismatch with the substrate. However, we can be confident of this correction factor. Selective excitation into the I_2 BE line reveals Ga as a dominant donor [Fig. 2(b)] from the displacement energy to the I_{2s}^{Ga} satellite. The I_{2o}^{Ga} energy is well established.[22] The same correction factor derived from the shift in I_2 moves the FE luminescence peak to the expected position near 2.8027 eV, and I_1^{N} to 2.792_0 eV essentially identical with Fig. 1(b). The key aspect of this observation is that Li is a much less significant contaminant in OMCVD ZnSe compared with LPE ZnSe, so that no I_1 line nor shallow DAP luminescence with no-phonon energy near 2.695 eV is observed in the absence of N.[21]

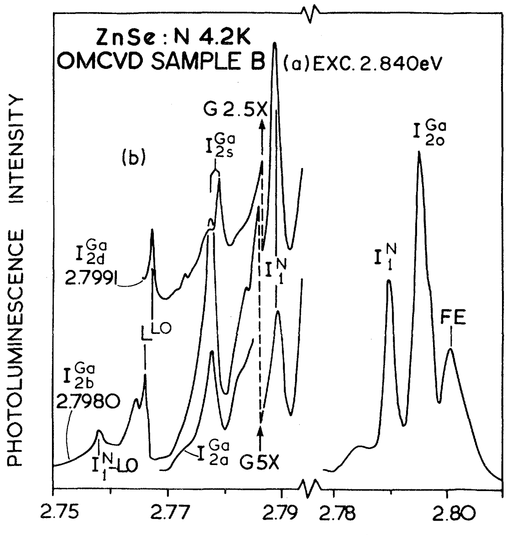

FIG. 2. Portions of near-gap photoluminescence from a heteroepitaxial crystal layer of ZnSe grown by OMCVD, sample B (OMCVD 2/5/82). (a) shows the FE and BE recorded under excitation energy above E_G. The energies are downshifted by ~2.5 meV due to strain between ZnSe and the GaAs substrate. (b) contains spectra recorded under selective excitation into the indicated different excited states of the D^0,X BE (see Fig. 1). I_1^{N} is the N A^0,X BE.

Information on the binding energies of shallow acceptors can be obtained from two-hole satellites of A^0,X BE.[14] These are best examined under selective excitation in the appropriate I_1 lines, so that the intensities of these weak satellites are boosted as much as possible relative to extraneous luminescence due to shallow DAP recombinations. Spectra for the selected LPE ZnSe:N crystal are compared in Fig. 3 for excitation at the (a) I_1^{Li} component and at (b) the I_1^{N} component. These spectra contain rather broad components displaced 82.4 meV below I_1^{Li} and 80.3 meV below I_1^{N}. The extreme width of two-hole BE satellites involving 2s-excited states is an endemic feature of shallow acceptors in ZnSe and is the subject of current theoretical study. Two-hole satellites

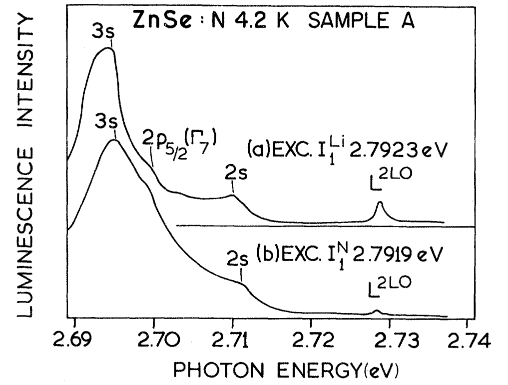

FIG. 3. Low-temperature photoluminescence spectra recorded for a ZnSe LPE homoepitaxial crystal, sample A, under selective excitation (a) in the Li and (b) in the N A^0,X BE lines. These spectra contain both broad low-energy luminescence from nonselectively excited DAP as well as additional rather narrower structures due partly to two-hole satellites of the A^0,X BE (see text).

involving $2p$-excited states are appreciably narrower in the purest available ZnSe despite their appreciably smaller binding energy.[9] This is not true in this particular LPE crystal, (Fig. 3), presumably a consequence of additional broadening of shallow energy states due to a significantly higher impurity concentration in these deliberately doped crystals. However, the relative values of the $1s \rightarrow 2s$ excitation energies obtained from these two-hole satellite energy shifts suggests that $(E_A)_{\mathrm{Li}} - (E_A)_{\mathrm{N}} \sim 2.1 \pm 0.7$ meV. We will find in Sec. III B that although this comparative technique provides a fair estimate for this energy difference, there is strong evidence that optical pumping of the A^0,X BE is rather inefficient and that DAP SPL effects make a major contribution to Fig. 3. Reasons for this are suggested in Sec. III C.

Further evidence of the difficulties with A^0,X BE SPL spectra in these thin n-type LPE crystals is provided from the prominence of the $2s$ two-hole satellite shown in Fig. 4(b), excited nonresonantly by strongly focused, weakly penetrating 3.41-eV laser light. The contrast of the $2s$ A^0,X BE replica is much larger than that achieved with dye-laser light at ~2.85 eV (poorer focus), with 2.807-eV light (more penetrating), or with A^0,X BE light. This sample is one of the most successful N-doped LPE layers available, with a negligible [Li]/[N] ratio and only a weak A^0,X BE line near 2.7937 eV [Fig. 4(a)]. The 2.7937-eV line is due to Na acceptors, as proved by the occurrence of a distant DAP peak about 17 meV below the dominant peak near 2.698 eV, due to N acceptors. The strength of phonon coupling to

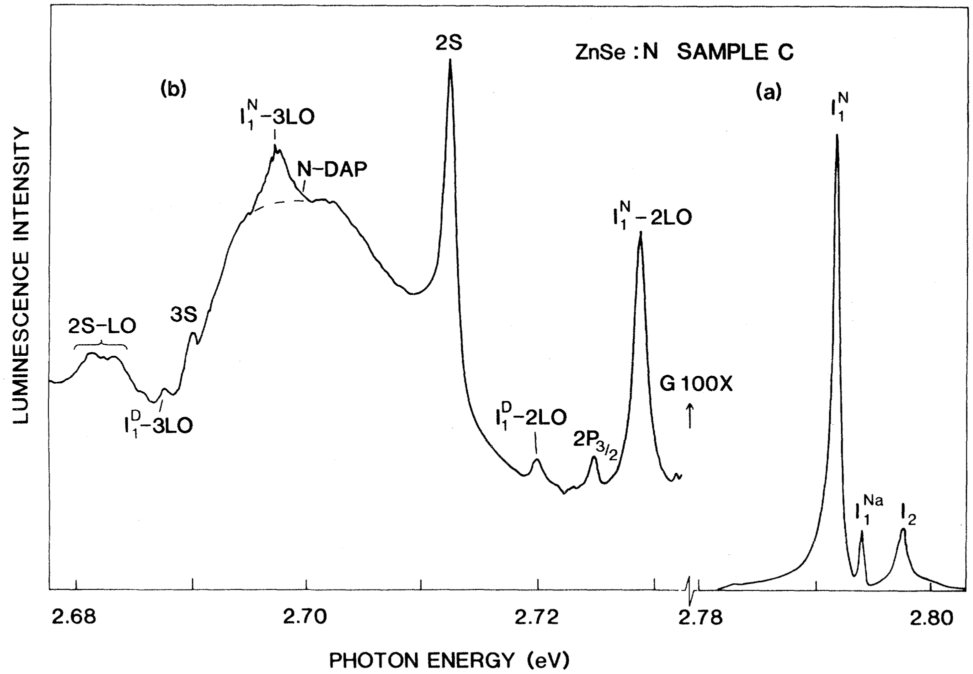

FIG. 4. Near-gap low-temperature photoluminescence from a predominantly N acceptor-doped single crystal of LPE ZnSe, sample C (708VA), recorded under intense above-band-gap excitation. The D^0,X (I_2) and A^0,X (I_1) BE are shown in (a), while (b) shows details near the distant DAP peaks involving N and Na acceptors. The two-hole BE replica involving transitions to the $2s$ state of the N acceptor and its broadened LO-phonon replica are of particular interest.

the deeper N A^0,X BE I_1^{N} is significantly larger than that for the Na A^0,X BE, I_1^{Na}, with Huang-Rhys coupling factors of ~0.09 and ~0.015, respectively. This stronger phonon coupling also applies to low-energy phonons, presumably responsible for the noticeably asymmetric line profile of I_1^{N}. Transitions to the 2*s*-acceptor excited state are expected to predominate in the two-hole satellite spectrum,[9] and are enhanced relative to the distant DAP transitions under the strong optical pumping. The identification of some of the weaker no-phonon structures in Fig. 4(b) is doubtful. The broad feature near 2.695 eV is only 9.8 meV below 2*s*, whereas the 2*s*-3*s* spacings for Li and Na acceptors are, respectively, 15.2 and 14.8 meV.[9] This feature may entirely be due to phonon replica I_1^{N}—3LO. However, the sharpest structure at 2.690 eV could be associated with the 3*s* transition of the N acceptor. The $2p_{3/2}$(?)-2*s* spacing in Fig. 4(b) is 12.7 meV, compared with 9.7 meV for Li and 10.8 meV for Na.[9] The LO-phonon replica of the 2*s* two-hole satellite of I_1^{N} exhibits a double-peaked structure with phonon energies of ~28.5 and ~30.7 meV and a Huang-Rhys factor ~0.5 for the entire doublet, comparable to the N DAP band in Fig. 5 as expected. The strong broadening, distortion of shape, and energy downshift relative to the normal LO(Γ) energy of the ZnSe lattice, 31.8 meV, are all consequences of the quantum-interference effect between bound and unbound LO phonons associated with the neutral acceptor. The effect is a consequence of the energy overlap between the electronic states represented by $(A_{2s}+\hbar\omega_{\mathrm{LO}})$ and (A^+ + free hole), as previously reported for shallow A^0,X BE in ZnTe.[24]

The displacement energy of the 2*s* satellite below I_1^{N} in Fig. 4 is 79.7 meV, 2.9 meV less than the corresponding energy for Li acceptors. We therefore conclude from all these A^0,X Be studies that $(E_A)_{\mathrm{N}}$ is about 111±1 meV, the error being largely governed by the uncertainty in binding energy of the 2*s* state of the acceptor. We now describe additional support for this small energy difference from the DAP SPL data.

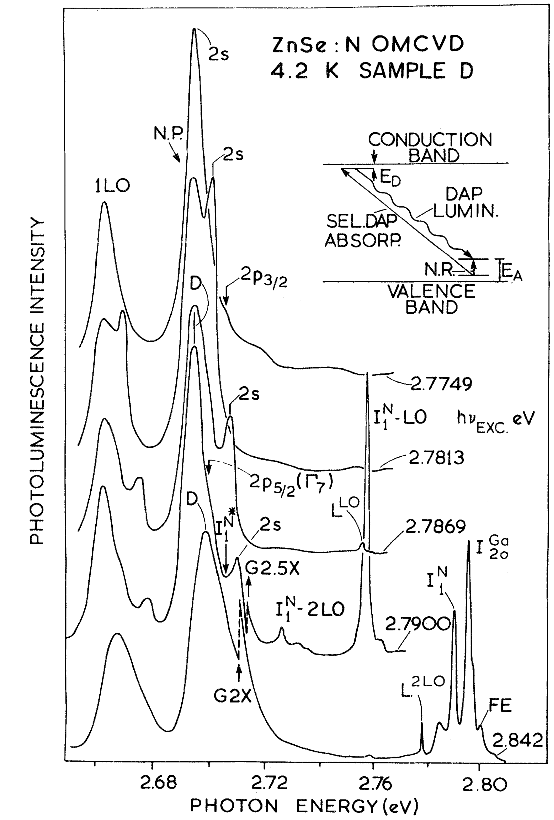

FIG. 5. Low-temperature DAP photoluminescence spectra from a ZnSe heteroepitaxial crystal grown by OMCVD, sample *D* (OMCVD 7/24/81), containing recombinations from nonselectively excited DAP involving *s* or *p* acceptor excited states. The mechanism for the selective DAP process is indicated in the inset. The spectra are recorded for the indicated photoexcitation energies. The lowest spectrum, recorded for excitation above E_G, contains no selectively excited DAP luminescence while *D* is both broader and shifted to higher energies. The DAP luminescence contains both no-phonon NP and LO phonon-assisted transitions.

B. Donor-acceptor—pair spectra

Nonselective excitation of DAP spectra involves the production of free-electron—hole pairs by above-band-gap light. These electronic particles are separately captured independently at compensated donors and acceptors. The resulting recombination luminescence provides evidence of the relative distribution of donors and acceptors among the available lattice sites of the crystal as a consequence of the well-known dependence of the transition energy *h* on the DAP separation *R*,

$$h\nu = E_G-(E_D+E_A)+e^2/\epsilon R \ ,$$

where E_G is the free-particle band gap, ϵ the static dielectric constant, and *e* the electronic charge. In favorable cases, rare for II-VI compounds such as ZnSe, DAP recombinations can be resolved from adjacent discrete values of *R*, permitting detailed information on E_D, E_A, the relative lattice sites they occupy, and their local symmetries.[25] More usually, only a broadened envelope of no-phonon transitions can be observed, even for those shallow DAP where phonon coupling is sufficiently weak to permit direct resolution of the no-phonon portion of the spectrum. However, it is possible to obtain direct information on the donor and acceptor members of the pair even when discrete DAP lines do not appear, through photoluminescence excitation (PLE) spectra or SPL. The latter technique has advantages[9] and was employed in the present work.

The basis of the SPL technique is explained in the inset to Fig. 5. Excitation within DAP of a particular separation R is achieved by matching the R-dependent absorption energy of these DAP to the energy of a tunable dye laser, such that the selected transition energy involves the creation of the neutral acceptor in an excited state, with the donor member of the DAP created in its ground state. Success of the technique depends upon recombination within the DAP before the excitation energy can diffuse to a different DAP. Internal deexcitation within the shallow acceptor is possible by very rapid nonradiative processes involving phonon emission, and the detected radiative recombination involves the acceptor ground state. The technique is limited to moderate doping levels such that energy diffusion between photoexcited DAP remains sufficiently slow, but this encompasses a considerable portion of the doping range of practical interest in many semiconductors, including the heaviest N doping so far achieved in ZnSe. The consequence of the SPL process is the appearance of relatively narrow luminescence bands involving recombinations within the resonantly excited DAP in addition to broader luminescence from DAP which have been nonselectively excited through parallel optical processes involving the generation of free carriers from compensated acceptors. The energies of the narrow bands are displaced from that of the exciting laser by excitation energies of the acceptor. The trade-off between the strong *increase* in oscillator strength of the intra-DAP absorption process and the *decrease* in the number of available DAP states with a decrease in R establishes a range of R over which the technique can be operated. In practice, this is characterized by the range of $h\nu_{\mathrm{exc}}$ over which the SPL satellite appears on the high-energy side of the intensity envelope of the DAP luminescence under nonselective excitation.[9] This remains true whether donor or acceptor excited states are involved. Thus quite different ranges of $h\nu_{\mathrm{exc}}$ are established for the study of shallow donor and acceptor excited states in a semiconductor like ZnSe, where $E_D \ll E_A$. Complications occur through the influence of intra-DAP interactions on the magnitudes of E_A (or E_D),[26,27] which introduces an R dependence significant for $R \lesssim 70$ Å for shallow DAP in ZnSe.[27] This is an important effect in the present work, since we are concerned with the establishment of a small energy shift between E_A^{N} and E_A^{Li}, comparable with the E_A produced by intra-DAP interactions for $R \lesssim 50$ Å.

The SPL spectra are compared in Fig. 5 with a nonselectively excited DAP spectrum (bottom, peak D), recorded with excitation energy well above the ZnSe band gap near 2.82 eV. Data for a second OMCVD crystal, grown nearly a year later, are very similar though the relative strength of the DAP luminescence compared with the BE and the BE intensity ratio $I_1^{\mathrm{N}}/I_{20}^{\mathrm{Ga}}$, both indicating a significantly smaller value of $\mathrm{N}_A/\mathrm{N}_D$ in the second crystal; N_A and N_D are the acceptor and donor concentrations, respectively. The question of the compensation level in these n-type crystals is discussed further in Sec. III C. There is no indication in Fig. 5 for the presence of inadvertent Li acceptors, for example, no high-energy shoulder appears on the I_1^{N} A^0,X BE line in contrast to Fig. 1(b) for LPE ZnSe. Three effects are evident in Fig. 5. First, the relative strength of the laser line (Raman) LO-phonon replica L^{LO} increases $\sim$tenfold when the laser is tuned into the A^0,X BE no-phonon line I_1^{N} compared with its value when $h\nu_{\mathrm{exc}}$ is ~ 3 meV lower. Second, the smooth, rather broadened DAP intensity envelope observed for $h\nu_{\mathrm{exc}} > E_G$ is replaced by a narrowed distribution with peak energy shifted ~ 4.5 meV to lower energy when $h\nu_{\mathrm{exc}}$ is kept below the strong absorption in this ~ 4-μm-thick crystal, which commences near I_{20}^{Ga} (Sec. III C). This is a normal property of a distant DAP spectrum in which transitions at discrete pairs remain unresolved, and is a consequence of the decrease in optical excitation density[25] as the exciting laser light becomes able to penetrate the whole epitaxial layer for $h\nu \lesssim I_{20}^{\mathrm{Ga}}$. The third effect is a well-defined shoulder on the high-energy side of the narrowed distant D. This shoulder maintains a separation of ~ 80 meV below the laser energy as $h\nu_{\mathrm{exc}}$ is reduced below I_1^{N}. Comparison with data for ZnSe:Li shows that this energy should be due to SPL absorption processes involving the $2s$ acceptor excited state (Fig. 5 inset), which predominates in the SPL or PLE spectra of ZnSe.[9] The crystal quality is not adequate to permit clear resolution of the much weaker transitions to other acceptor excited states. However, weak shoulders consistent with the expected positions of the $2p_{5/2}(\Gamma_7)$ and $2p_{3/2}$ excited states appear in spectra for $h\nu_{\mathrm{exc}}$, respectively, equal to 2.7900 and 2.7749 eV. The origin of the further broad, weak structure at higher energy in the spectrum for $h\nu_{\mathrm{exc}} = 2.7749$ eV is uncertain. These spectra also contain the one-LO-phonon replicas of these DAP features.

The energy displacements of the $2s$ SPL satellites in two ZnSe:N OMCVD crystals are compared in Fig. 6 with those from a conventional vapor-transport single crystal containing Li, reported by Tews *et al.*[9] Despite the significant scatter associated with measurements on such broad features, it is

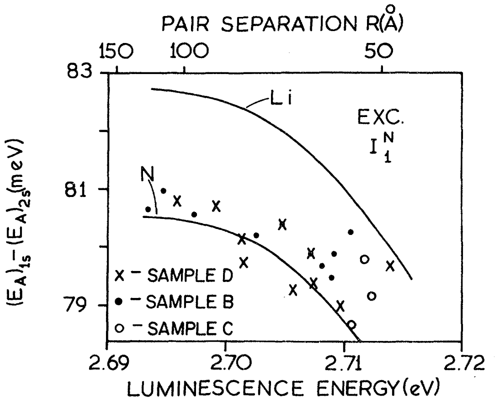

FIG. 6. Variation of the peak displacement energies of the principal satellite in the selectively excited DAP photoluminescence spectra for both Li acceptors (upper line from Ref. 9, no experimental points shown for clarity) and N acceptors. Data were obtained for the indicated three crystals. The 1*s*→2*s* displacement energy is plotted against the energy of the DAP luminescence line, equivalent to the DAP separation *R* shown at the top. The downward trend of the 1*s*-2*s* separation with decreasing *R* arises from the influence on the *A* energies of the nearby *D*. Anomalies occur near 2.713 eV, the luminescence energy where some contribution is obtained from A^0,X BE two-hole satellites.

clear that the trend of the data gives a 1*s*-2*s* acceptor energy separation consistently less for the N acceptor compared with Li, by about 2.2±0.5 meV, in agreement with conclusions from BE spectra (Sec. III A). This is consistent within experimental error with the estimate $(E_A)_{\mathrm{N}}=111\pm1$ meV from the A^0,X BE data in Sec. III A. The close values of $(E_A)_{\mathrm{N}}$ and $(E_A)_{\mathrm{Li}}$ and the insensitive, slightly retrograde dependence of E_{BX} on E_A suggests[14] that $(E_A)_{\mathrm{EMT}}$ may be close to 110 meV in ZnSe. This compares favorably with the behavior of acceptors from the first row of the Periodic Table in other semiconductors, for example, B in Si and C in GaAs and GaP (Ref. 28), and is consistent with simple predictions from differential electronegativity. The theoretical value $(E_A)_{\mathrm{EMT}}$ for ZnSe is 110 meV according to Baldereschi and Lipari,[29] in excellent agreement with the conclusion from our experimental data. However, this agreement may be slightly fortuitous since the theoretical value for $(E_A)_{\mathrm{EMT}}$ in ZnTe reported by Baldereschi and Lipari[29] is ~78 meV, substantially in excess of the value consistent with accurate experimental data,[30] $(E_A)_{\mathrm{EMT}}\sim 60$ meV. The main reason for this discrepancy is the use of inappropriate valence-band parameters for ZnTe. The present estimate $(E_A)_{\mathrm{EMT}}=110$ meV for ZnSe is appreciably larger than values previously reported for the shallowest acceptors in ZnSe,[4,13] which is very surprising.

C. Photoluminescence excitation spectra

The absence of any clear additional satellite when $h\nu_{\mathrm{exc}}$ is tuned into I_1^{N} (Fig. 5) indicates that even for this resonant condition the main luminescence excitation channel involves the photoneutralization of distant DAP rather than the creation of the A^0,X BE. The latter process should be marked by a two-hole satellite of the I_1^{N} line displaced by *exactly* the 1*s*→2*s*-acceptor excitation energy as in Fig. 4, since these transitions occur preferentially at acceptors which lie far from donors rather than the relatively small separation $R\sim 50$ Å, indicated in Fig. 6 for the DAP absorption process when $h\nu_{\mathrm{exc}}$ is tuned to I_1^{N}. The expected satellite position is about 3.9 meV below the DAP SPL satellite, denoted by $I_1^{\mathrm{N}*}$ in Fig. 5. No secondary peak is resolved at this energy. However, the dip between the SPL 2*s* shoulder and the main distant DAP peak is considerably shallower for $h\nu_{\mathrm{exc}}=2.7900$ eV compared with $h\nu_{\mathrm{exc}}=2.7869$ eV, too low for efficient A^0,X BE optical pumping.

More insight concerning optical excitation processes in these crystals is obtained from the PLE spectra in Fig. 7. When the D^0,X BE two-electron satellite is detected, the PLE spectrum contains a very strong peak at I_{20}^{Ga}, with poorly resolved structure from the expected excited states below the $n=1$ FE and little else. The response from the I_1^{N} line is weak, indicating little BE tunneling from A^0 to D^0 as expected for this anti-Stokes process at 4.2 K. The broad dip at the $n=1$ FE is an expected consequence of strong surface recombination.[22] No features appear at the expected positions I_{20}^* and $I_{2c,d}^*$ for D^0,X BE excited states associated with the $n=2$ FE,[22] presumably because of rapid energy transfer to the lowest D^0,X BE states enhanced by interdonor cross-relaxation processes which are clearly very strong in these crystals. In these processes, the D^0,X BE excitation energy represented by $I_{2c,d}-I_{20}\sim 19.2\pm0.5$ meV can be given to a neighboring neutral donor, promoting the excitation $1s\rightarrow 2s,2p\sim 20$ meV. In fact, this conjecture is supported by SPL spectra recorded for resonant excitation at these energies, which are dominated by I_{20}^{Ga} with no detectable two-electron satellites, in sharp contrast to the behavior of more lightly doped crystals.[22]

The PLE of the DAP SPL satellite 2*s* at 2.7103 eV corresponding to the $h\nu_{\mathrm{exc}}=2.7900$ eV spectrum in Fig. 5 contains negligible contributions from I_1^{N} or I_{20}^{Ga}. Indeed, there is some evidence of a dip due to the latter, as expected since I_{20}^{Ga} luminescence is moderately efficient and is not detected in this experiment. The main near-gap feature is a broad excitation band with a well-defined threshold near

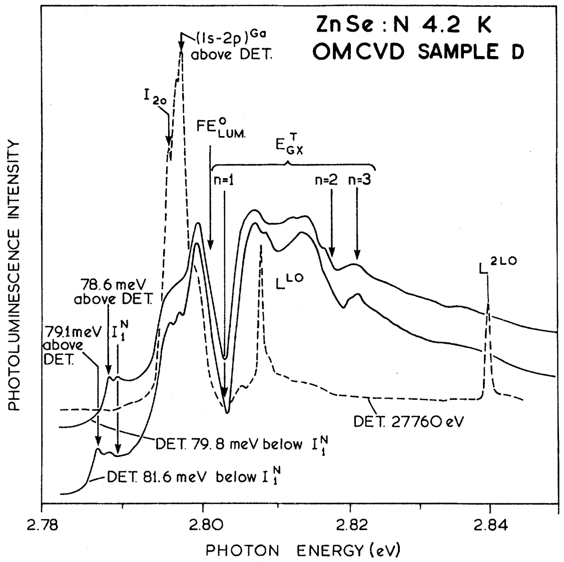

FIG. 7. Low-temperature photoluminescence excitation spectra recorded for an OMCVD grown heteroepitaxial ZnSe crystal (sample *D*) for the three indicated detection energies. Components L^{LO} and $L^{2\mathrm{LO}}$ are due to vibronic Raman scattering. Note that no significant contribution appears at the I_1^{N} A^0,X BE even when the detector is set at the 1*s*-2*s* isolated N acceptor excitation energy below it (see text). The transverse FE energies E_{GX}^T are indicated for various orbital states, $n=1\rightarrow3$. The dashed curve is obtained for detection at the 1*s*-2*p* two-electron satellite of I_{2b}^{Ga}.

$h\nu=E_G-E_D^{\mathrm{Ga}}$, with a superimposed negative structure associated with FE absorption and a strong positive response extending well above E_G. This clearly shows that the distant DAP recombination process is favored by creation of free-electron—hole pairs rather than by BE or FE and confirms that the 2.7103-eV peak results from DAP SPL recombinations rather than A^0,X BE processes.

The effects in Fig. 7 contrast strongly with ZnTe, where D^0,X BE processes can be clearly observed in photoluminescence and PLE spectra, even for crystals back doped to $\mathrm{N}_A-\mathrm{N}_D\sim10^{16}$ cm^{-3}. The difference is a characteristic of the reverse situation which obtains in these ZnSe crystals $\mathrm{N}_D-\mathrm{N}_A\sim10^{16}$ cm^{-3} with compensation enhanced by the introduction of shallow N acceptors though still probably not severe. No evidence of *p*-type conductivity has yet been obtained in these N-doped OMCVD crystals.[21] They are all either high resistivity or *n* type. The contrasting behavior is associated with the much greater tunneling rates associated with electrons bound to 26-meV donors in ZnSe, radius 30 Å, compared with holes bound to ∼60-meV acceptors in ZnTe, radius 11 Å, contrasted for $\mathrm{N}_D,\mathrm{N}_A\sim10^{16}$ cm^{-3}. The point is that the distant DAP recombination rate is critically governed by the concentration of the shallow radius (*D*) member of the pair. Thus it makes a great difference whether *D* or *A* are in excess at a given concentration. The DAP recombination channel is very much more effective in competition with BE processes in these ZnSe crystals compared with ZnTe. In the latter case, it is relatively easy to promote strong two-electron BE satellites by resonant excitation at D^0,X BE (I_2) even when $\mathrm{N}_A\gg\mathrm{N}_D$ and $\mathrm{N}_A\sim10^{16}$ cm^{-3}. However, it is much more difficult to promote two-hole BE satellites under the reverse conditions in ZnSe for resonant excitation within I_1^{N}. The contrast is abetted by the lower oscillator strength of I_1^{N} compared with $I_{2\mathrm{o}}^{\mathrm{Ga}}$ (Ref. 31) and by the weaker continuum absorption for the valence band (VB)→*D* absorption process at I_1 needed for acceptor neutralization in ZnSe compared with the *A*→conduction band (CB) process at I_2, needed for donor neutralization in ZnTe. In fact, as shown in Fig. 7, I_1 lies just below threshold energy (E_G-E_D) for the VB→*D* process, whereas no such problem occurs for the *A*→CB process. We conclude that the most efficient method for promoting A^0,X BE luminescence in *n*-type ZnSe involves the production of free-electron—hole pairs at high-optical excitation rates, as in Fig. 4.

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